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Programmable Assembly of Nanomaterials Using Biopolymers : Supplemantary Materials

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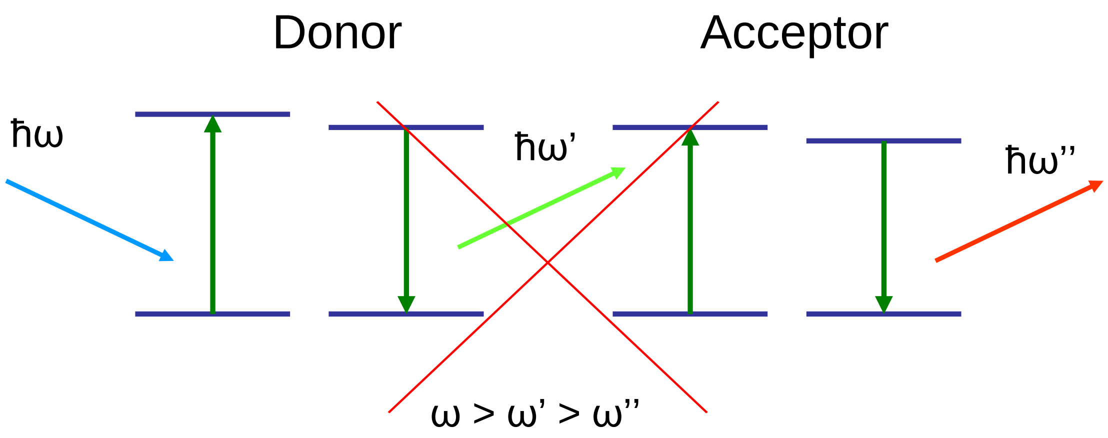
Fluorescence Resonance Energy Transfer (FRET)

- FRET is a photophysical process involving a donor molecule and an acceptor molecule
- The donor molecule is optically excited and transfers some of its excitation energy to the acceptor molecule
- The transfer mechanism decreases the fluorescence lifetime of the donor molecule



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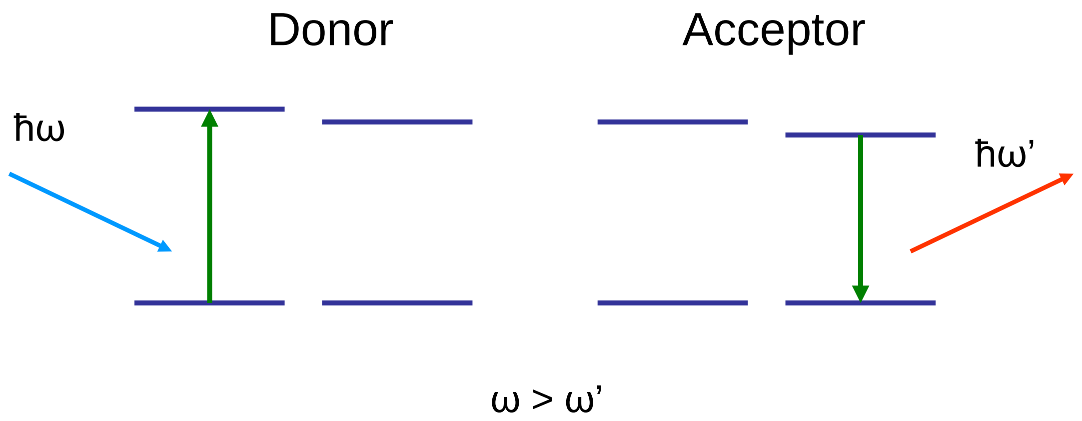
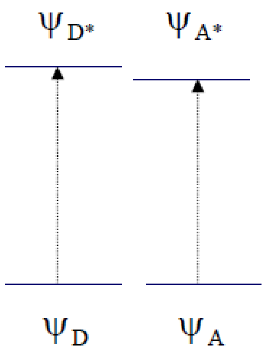


Fluorescence Resonance Energy Transfer (FRET)

$$H = H_D + H_A + H_{int},$$

$$\psi_i = \frac{1}{\sqrt{2}}\left(\psi_{D^*}(1)\psi_A(2) - \psi_{D^*}(2)\psi_A(1)\right),$$

$$\psi_f = \frac{1}{\sqrt{2}}\left(\psi_D(1)\psi_{A^*}(2) - \psi_D(2)\psi_{A^*}(1)\right),$$



$$H_{if} = <\psi_i \mid H_{int} \mid \psi_f>$$
$$= \left\langle \psi_{D^*}(1)\psi_A(2) \mid H_{int} \mid \psi_D(1)\psi_{A^*}(2)\right\rangle - \left\langle \psi_{D^*}(1)\psi_A(2) \mid H_{int} \mid \psi_D(2)\psi_{A^*}(1)\right\rangle$$

Columbic - Long range interaction

Forster Mechanism

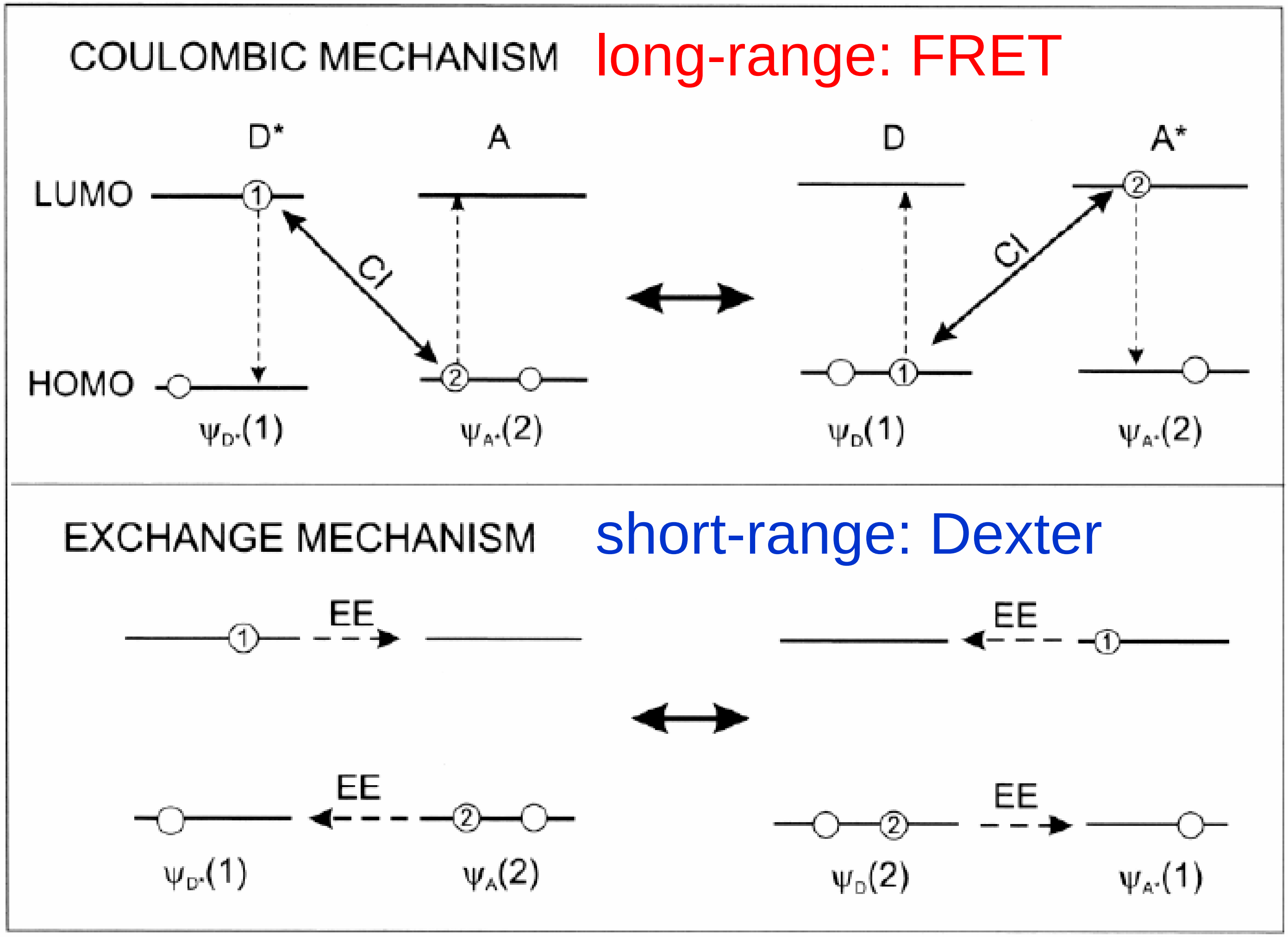
Pure classical analog

Exchange - Short range interaction

Dexter Mechanism

Exponential distance (instead of r^6) dependence
Operational for dipole forbidden transitions

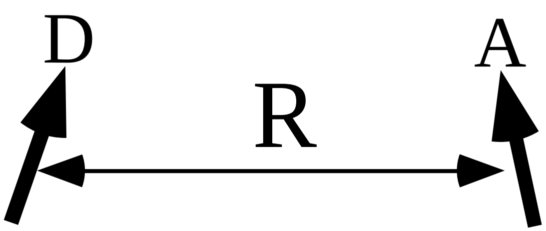
Fluorescence Resonance Energy Transfer (FRET)

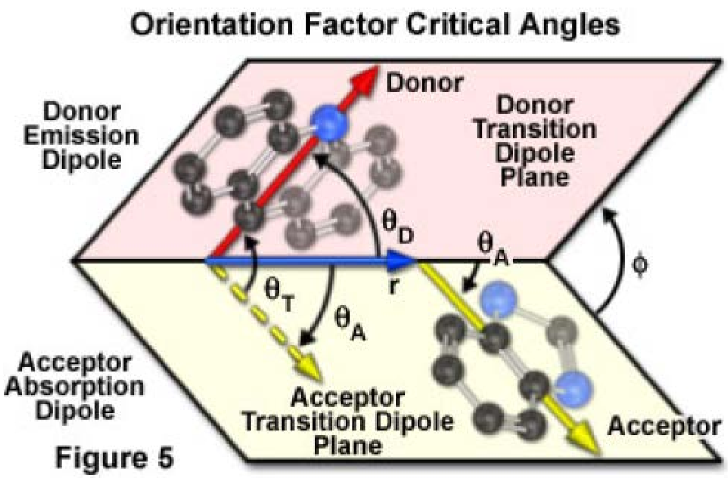


Inter-molecular orbital overlap

Fluorescence Resonance Energy Transfer (FRET)

Two oscillating dipoles





Electric field of D:

$$\mathbf{E}_D = [3(\boldsymbol{\mu}_D \cdot \mathbf{R})\mathbf{R}/R^2 - \boldsymbol{\mu}_D]/n^2R^3$$

Energy of interaction :

$$E_{int} = -\boldsymbol{\mu}_A \cdot \mathbf{E}_D = [\boldsymbol{\mu}_A \cdot \boldsymbol{\mu}_D - 3(\boldsymbol{\mu}_A \cdot \mathbf{R})\,(\boldsymbol{\mu}_D \cdot \mathbf{R})/R^2]/n^2R^3$$

$$= \kappa\mu^2/n^2R^3\,, \qquad \text{if } |\boldsymbol{\mu}_A| = |\boldsymbol{\mu}_D| = \mu$$

Orientation factor: $\kappa = \cos\theta_T - 3\cos\theta_D\,\cos\theta_A$

Fluorescence Resonance Energy Transfer (FRET)

$$k = \frac{2\pi}{\hbar} \left| V^{Coul} \right|^2 \int_0^\infty J(E) dE$$

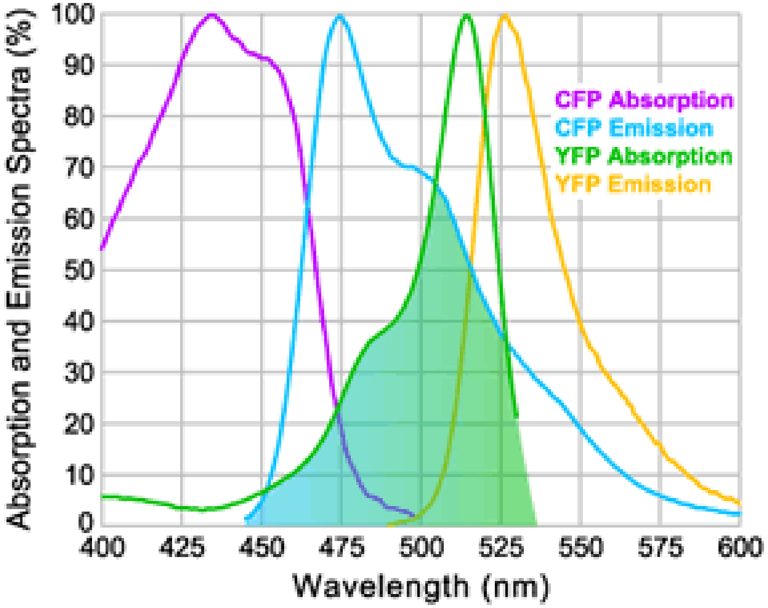
where $\mathrm{J(E) = f(E)}\alpha\mathrm{(E)}$

f(E) : normalized donor fluorescence

α(E) : the normalized acceptor absorption

Define Forster spectral integral I :

$$I = \int_0^\infty J(E) dE \quad \left(cm^3 / M \right)$$



Fluorescence Resonance Energy Transfer (FRET)

$$k = \frac{1}{\tau_D}\,\frac{\kappa^2 \Phi_D I}{n^4}\,\frac{1}{R^6}\left(\frac{9000(\ln 10)}{128\pi^5 N}\right)$$

τ_D = donor lifetime

κ = orientation factor

Φ_D = donor fluorescence quantum yield

I = spectral overlap

n = index of refraction of medium

R = center to center separation

N = Avogadro's number

Energy transfer rate:

$$k = (R_0/R)^6/\tau_D$$

Förster constant (radius):

$$R_0 = c_0\,\kappa^2 I\, n^{-4}\, \Phi_D$$

Energy transfer efficiency:

$$E = k \cdot \tau = (R_0/R)^6/[1+(R_0/R)^6]$$

$$\tau_D^{-1} = k_f + k_{nr} + k_{isc} + k_{pb}$$

$$\tau^{-1} = \tau_D^{-1} + k$$

$$\kappa^2 = (\cos\theta_T - 3\cos\theta_D \cos\theta_A)^2$$

= 2/3 for the random orientation

Fluorescence Resonance Energy Transfer (FRET)

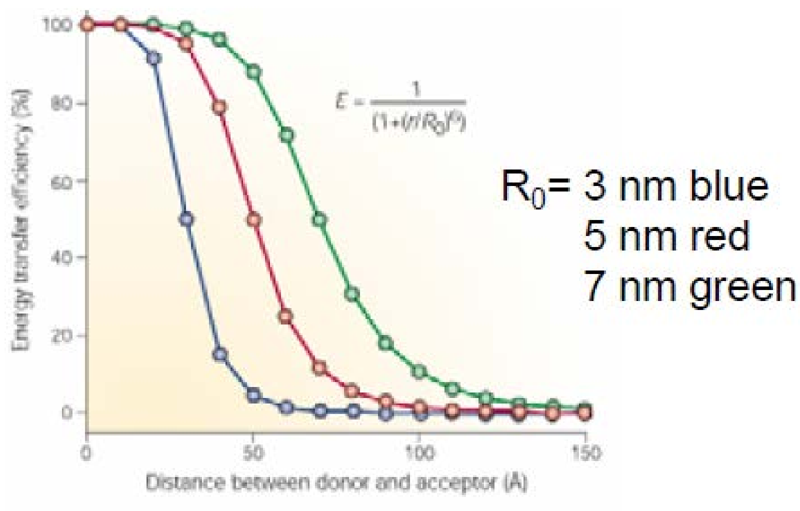
$$k = \frac{1}{\tau_D} \frac{\kappa^2 \Phi_D I}{n^4} \frac{1}{R^6} \left(\frac{9000(\ln 10)}{128\pi^5 N} \right)$$

$$k = (R_0/R)^6/\tau_D$$

$$R_0 = c_0\, \kappa^2\, I\, n^{-4}\, \Phi_D$$

$$E = k \cdot \tau = (R_0/R)^6/[1+(R_0/R)^6]$$

$$\kappa^2 = (\cos\theta_T - 3\cos\theta_D \cos\theta_A)^2$$



Ruler (only) works near R_0

- The donor quantum yield (>0.5)
- The index of refraction (1/3-1/5)
- The spectral overlap (0.1-0.5)
- The orientation of the dipoles (0-4)

Plasmonics

The Lycurgus Cup (glass; 4th century)

When illuminated from outside, it appears green. However, when Illuminated from within the cup, it glows red. Red color is due to very small amounts of gold powder (about 40 parts per million) embedded in the glass, which have an absorption peak at around 520 nm.

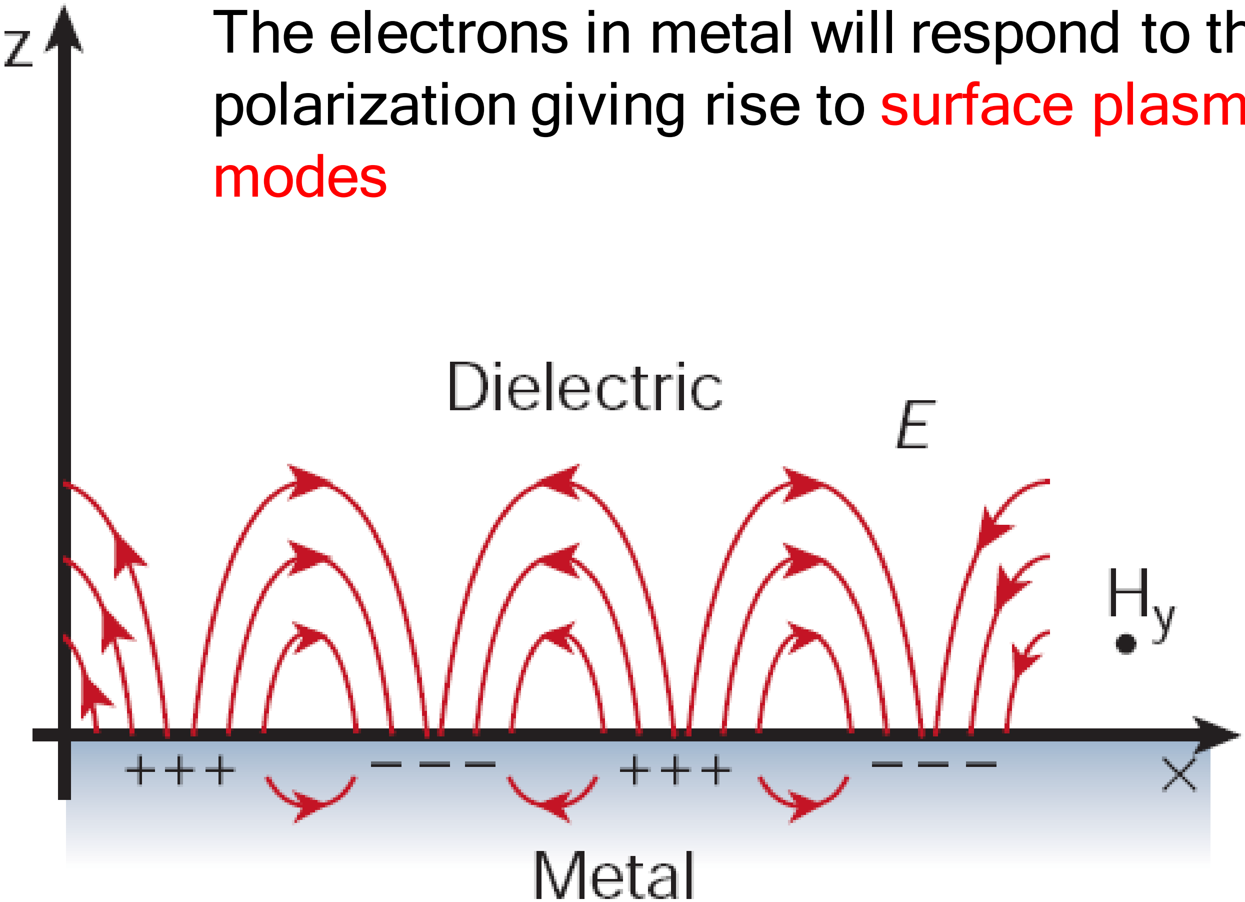
Stained Glass Windows

Plasmon resonances give specific metallic nanoparticles a strong and well defined color. This effect was already used in the Middle Ages to fabricate stained-glass windows.

Plasmonics

Polarization charges are created at the interface between two material.

The electrons in metal will respond to this polarization giving rise to surface plasmon modes



Plasmonics

What is the wavelength of the surface plasmon $\lambda = \dfrac{2\pi}{k}$?

let us find *k:*

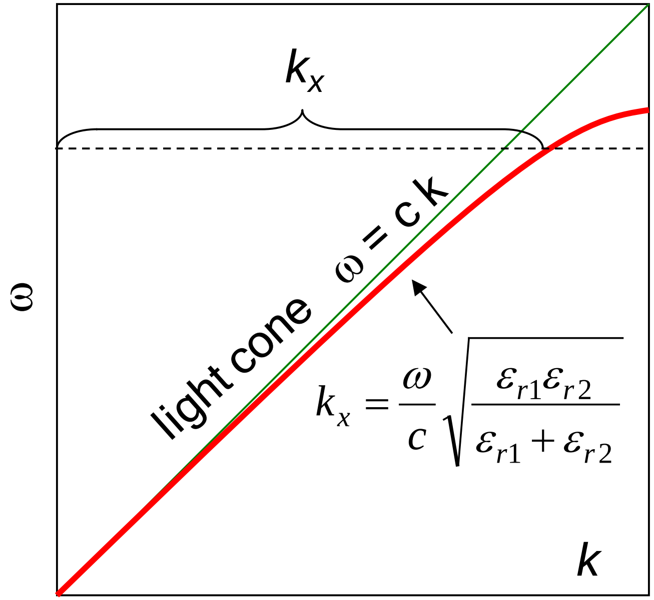
$$\frac{\varepsilon_{r1}}{k_{1z}} = \frac{\varepsilon_{r2}}{k_{2z}}$$

substitute

$$k_{1z} = -\sqrt{(n_1 k)^2 - k_{1x}^2}$$

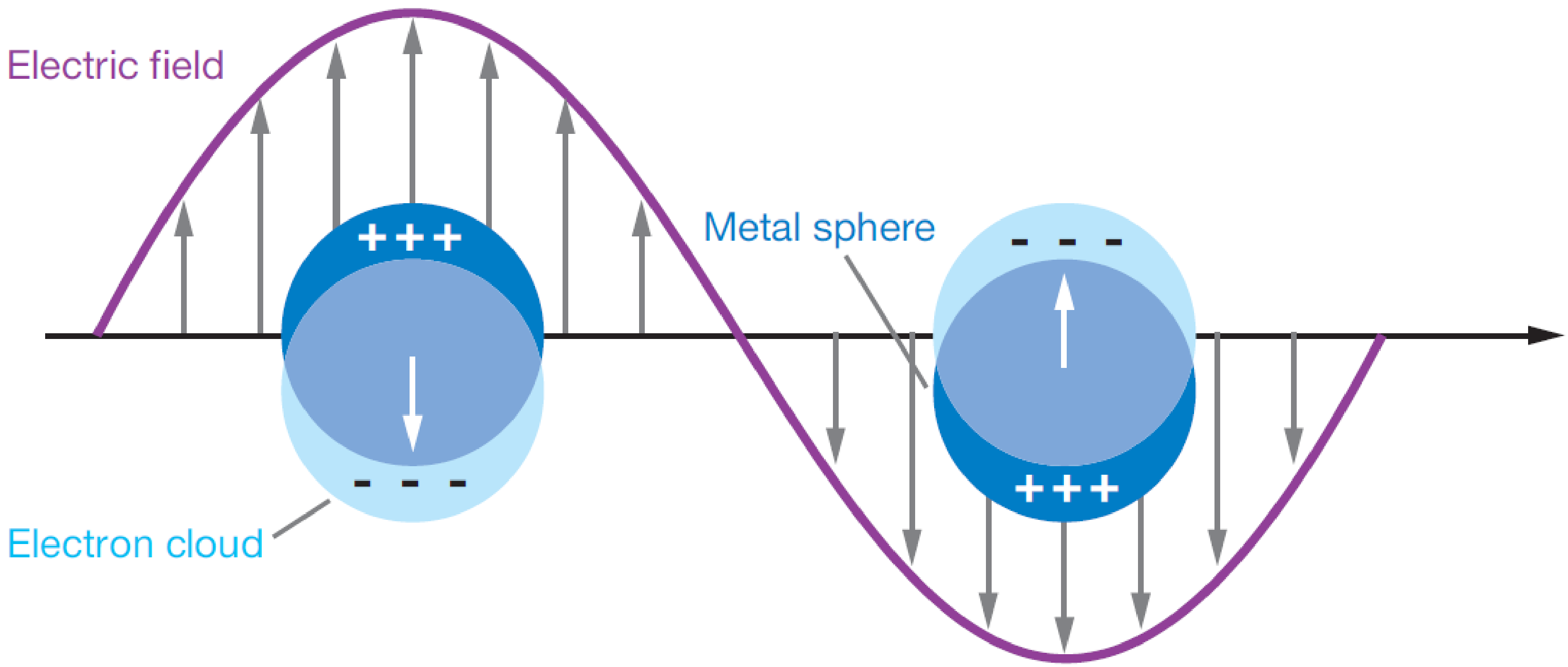
$$k_{2z} = +\sqrt{(n_1 k)^2 - k_{2x}^2}$$

$$k_x = k\sqrt{\frac{\varepsilon_{r1}\varepsilon_{r2}}{\varepsilon_{r1} + \varepsilon_{r2}}}$$



The surface plasmone mode always lies beyond the light line, that is it has greater momentum than a free photon of the same frequency ω

Plasmonics

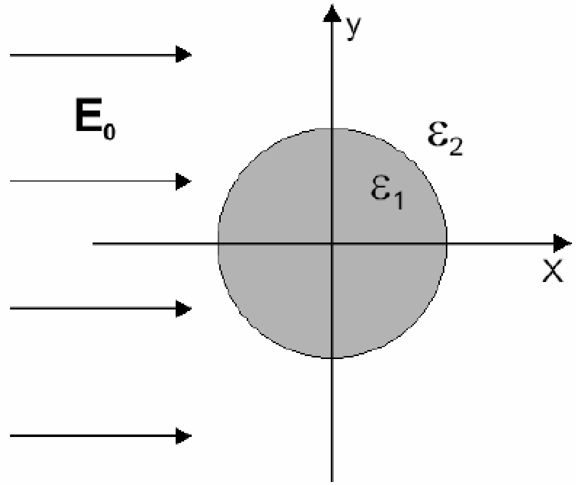


condition for plasmonic resonance:

metall → $\varepsilon'(\omega) = -2\varepsilon_m$ ← host dielectric material

Plasmonics

Quasi-static Approximation:



Electrostatics problem

$$\frac{1}{r^2 \sin\theta}\left[\sin\theta\frac{\partial}{\partial r}\left(r^2\frac{\partial}{\partial r}\right)+\frac{\partial}{\partial\theta}\left(\sin\theta\frac{\partial}{\partial\theta}\right)+\frac{1}{\sin\theta}\frac{\partial^2}{\partial\varphi^2}\right]\Phi(r,\theta,\varphi)=0$$

Plasmonics

$$\Phi_1 = -E_0 \frac{3\varepsilon_2}{\varepsilon_1 + 2\varepsilon_2} r \cos\theta$$

$$\Phi_2 = -E_0 r \cos\theta + E_0 \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + 2\varepsilon_2} a^3 \frac{\cos\theta}{r^2}$$

$$\mathbf{E} = -\nabla\Phi \quad \Rightarrow$$

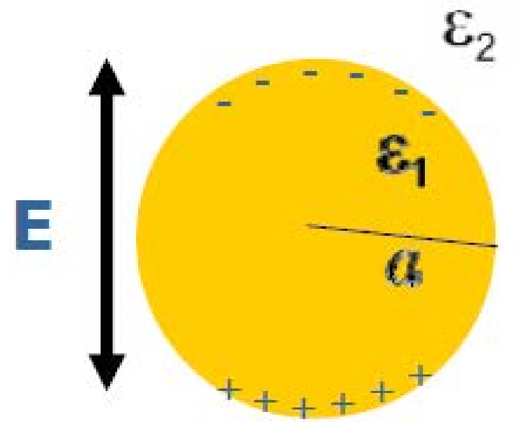
$$\mathbf{E}_1 = E_0 \frac{3\varepsilon_2}{\varepsilon_1 + 2\varepsilon_2} (\cos\theta\, \mathbf{e}_r - \sin\theta\, \mathbf{e}_\theta) = E_0 \frac{3\varepsilon_2}{\varepsilon_1 + 2\varepsilon_2}\, \mathbf{e}_x$$

$$\mathbf{E}_2 = E_0(\cos\theta\, \mathbf{e}_r - \sin\theta\, \mathbf{e}_\theta) + \frac{\varepsilon_1 - \varepsilon_2}{\varepsilon_1 + 2\varepsilon_2} \frac{a^3}{r^3} E_0 \left(2\cos\theta\, \mathbf{e}_r + \sin\theta\, \mathbf{e}_\theta\right)$$

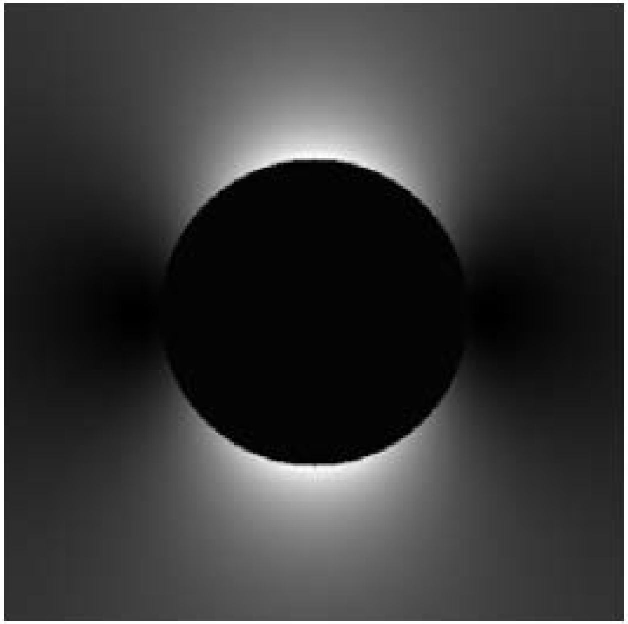
Plasmonics

Quasi-static limit:

Particles smaller than the skin depth of metal



Field enhancement is determined only by the material properties, not the size of the particle - but smaller particles give more confinement



$$\boldsymbol{\mu} = \varepsilon_2 \alpha(\omega) \mathbf{E}_0$$

$$\alpha(\omega) = 4\pi\varepsilon_o a^3 \frac{\varepsilon_1(\omega) - \varepsilon_2}{\varepsilon_1(\omega) + 2\varepsilon_2}$$

Plasma resonances for various geometries

Material	Resonance condition	Resonance Frequency
Bulk Metal	$\varepsilon_{eff} = 0$	ω_p
Planar Surface	$\varepsilon_{eff} = -\varepsilon_d$	$\frac{\omega_p}{\sqrt{2}}$
Sphere	$\varepsilon_{eff} = -2\varepsilon_d$	$\frac{\omega_p}{\sqrt{3}}$
Ellipsoid	$\varepsilon_{eff} = -\frac{1-L_M}{L_M}$	$\omega_p L_M$

Optical Properties of Metal Clusters
Kreibig and Vollmer,1995